New High-Energy Electrochemical Couple for Automotive Applications

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DOE merit review

June 6th ~10th , 2016

Project ID: ES208

Overview

Timeline

- Start - October 1st, 2013.
- Finish - September 30, 2015.
- 100% Completed

Barriers

- Barriers addressed
  - High energy (>200wh/kg)
  - Long calendar and cycle life
  - Abuse tolerance

Budget

- Total project funding
  - DOE share: 2500K
- Funding received in FY13: 1250K
- Funding for FY14: $1250K

Partners

- Project lead: Khalil Amine
- Interactions/ collaborations:

- **X. Q. Yang (BNL)** diagnostic of FCG cathode and SEI of Si-Sn composite anode
- **G. Liu (LBNL)** development and optimization of conductive binder for Si-Sn composite anode
- **ECPRO:** provide baseline cathode material
- **Utah University:** provide facility to scale up the baseline Si-Sn composite anode for baseline cell
- **Andy Jansen & Polzin, Bryant (ANL)** fabrication of baseline cell
- **Paul Nelson (ANL)** design of cell using BatPac

Relevance and project Objectives

- Objective: develop very high energy redox couple (250wh/kg) based on high capacity full gradient concentration cathode (FCG) (230mAh/g) and Si-Sn composite anode (900mAh/g) with long cycle life and excellent abuse tolerance to enable 40 miles PHEV and EVs

- This technology, If successful, will have a significant impact on:
  - *Reducing battery cost and expending vehicle electrification*
  - *Reduce greenhouse gases*
  - *Reduce our reliance on foreign oil*

Milestones

- March 2015:
  - Improve efficiency of SiO-SnCoC anode to over 80% (completed)

- August 2015:
  - Finalize the Optimization of the processing of SiO-SnCoC-MAG to get uniform electrodes and demonstrate up to 100 cycles of SiO-SnCoC-MAG using new LiPAA binder (completed)

- September 2015:
  - Optimize and scale up of Improve further FCG cathode with 210mA/g at 4.5V (**completed**).
  - Provide FCG cathode (1Kg) to CAM facility for cell design and build (completed)
  - Supply 14 cells to INL for testing and validation (completed)

Approach

ANODES

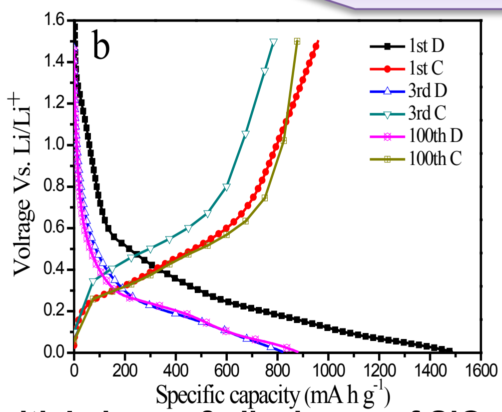
$SiO-Sn_yCo_{1-x}Fe_xC_z$ composite coupled with conductive binder

ELECTROLYTES

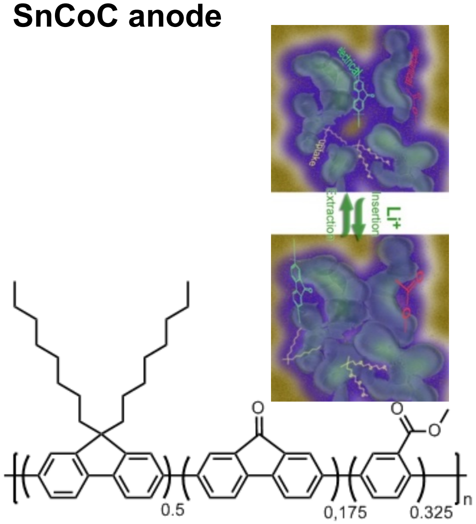
High voltage electrolytes with additives to stabilize interface of cathode and anode

CATHODES

Full Gradient concentration (FCG) $LiNi_xMn_yCo_zO_2$ with high concentration of Mn at the surface of the particle

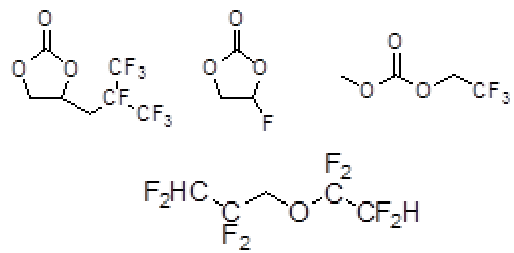


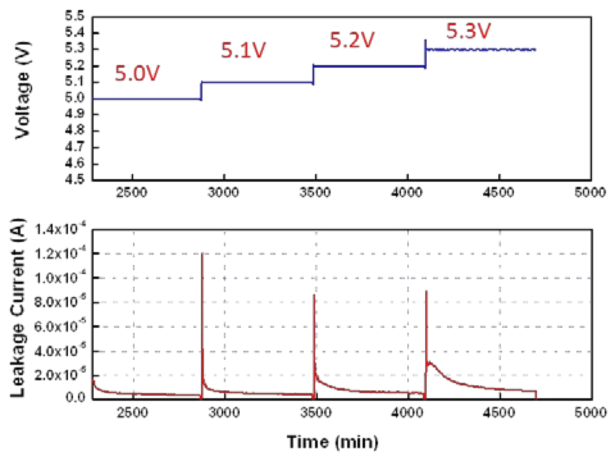
Initial charge & discharge of SiO-SnCoC anode



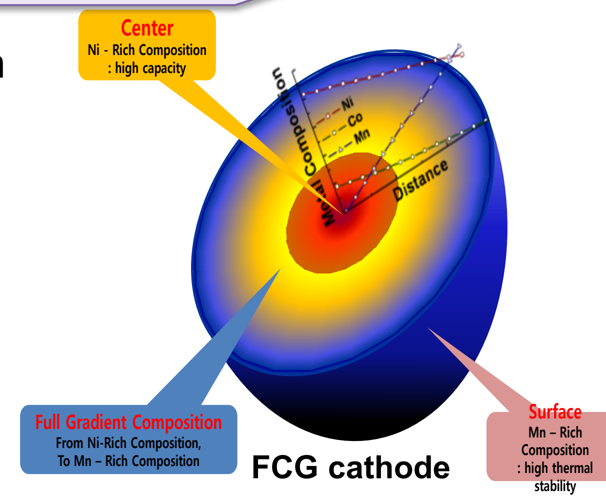
Conductive binder

Fluorine based electrolyte with additives:

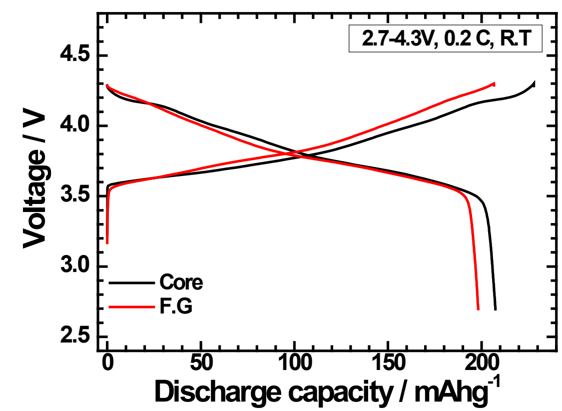




Floating test at different voltages of $LiNi_{0.5}Mn_{1.5}O_4/Li_4Ti_5O_{12}$ Cell using fluorinated electrolyte



FCG cathode



Initial charge & discharge of FCG cathode

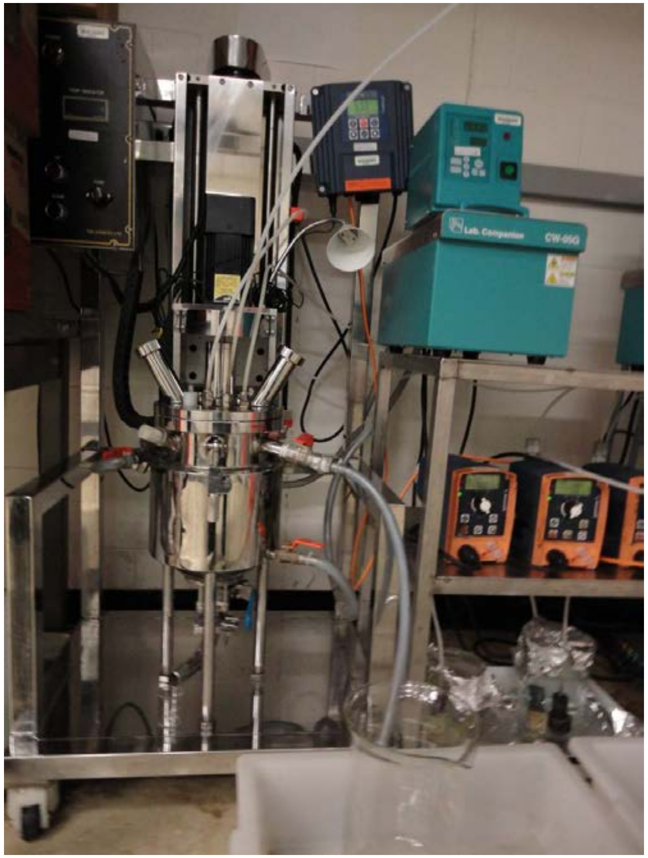
Technical accomplishments

- Optimized the process of making FCG cathode and demonstrate capacity as high as 210mAh/g with 2.7 tap density
- Characterized the FCG material using soft and hard X-ray in collaboration with BNL
- Scaled up FCG cathode to 1Kg level for electrode making using CAMP facility at Argonne
- Build cells based on FCG cathode and graphite anode and demonstrate good cyclability at high voltage
- Developed a new prelithiation process to eliminate the large initial irreversible loss of SiO-SnCoC anode

FCG Cathode development approach

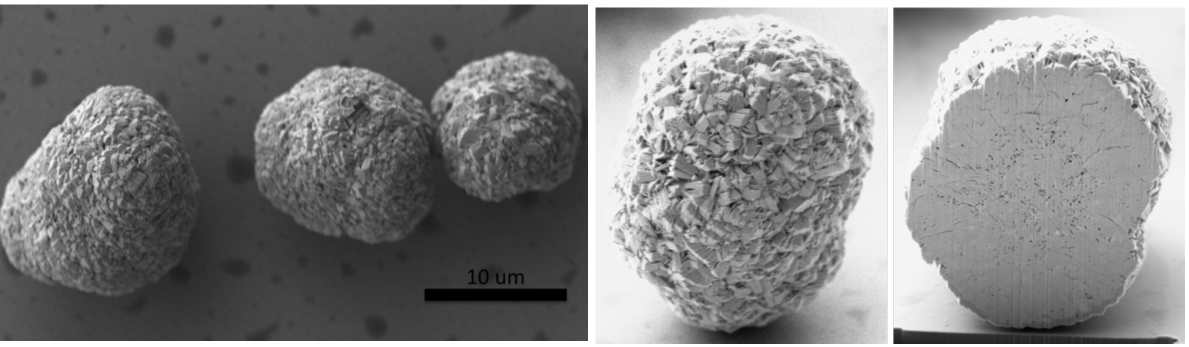
1. Design of full concentration gradient cathode material
2. Preparation of full concentration gradient (FCG) precursor via CSTR Co-precipitation with optimized condition
3. Calcination of FCG cathode with optimized condition
4. Physical characterization
5. Electrochemical evaluation

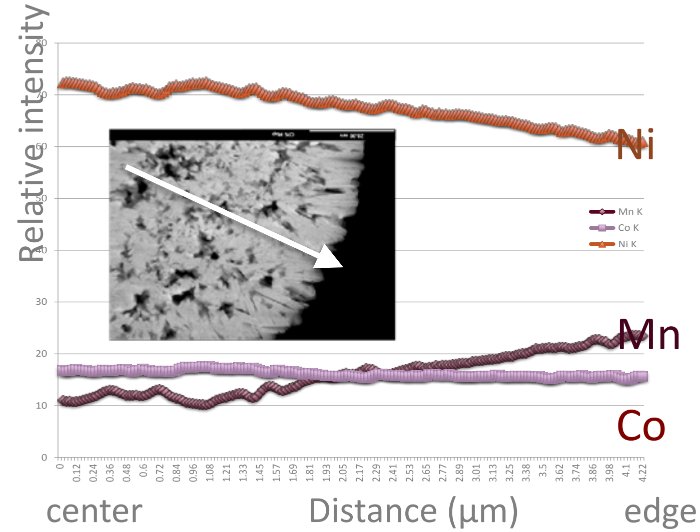
FCG material design
↓
Optimize the precursor
↓
Optimize the calcination
↓
Characterization (XRD, SEM, TEM)
↓
Electrochemical evaluation (coin cell)
↓
CFF for pouch cell evaluation



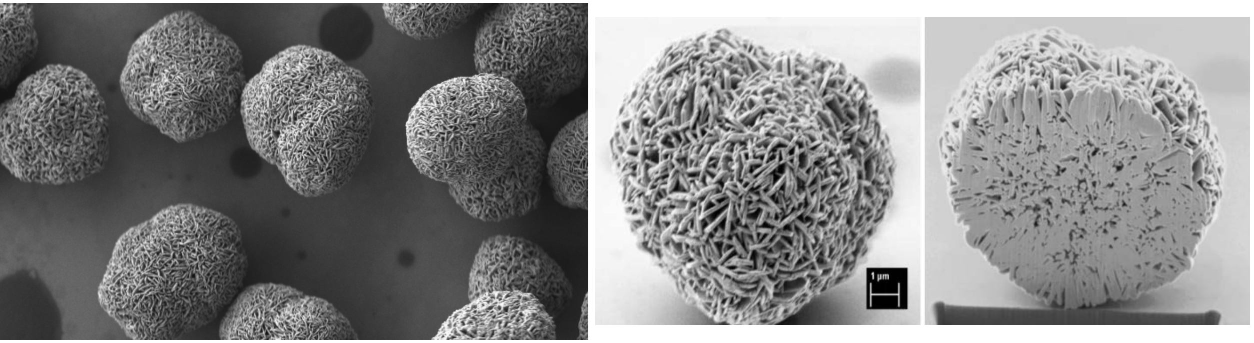
Reactor Setup

Characteristics of FCG gradient precursor & final active material made from hydroxide process after optimization





$Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)_2$



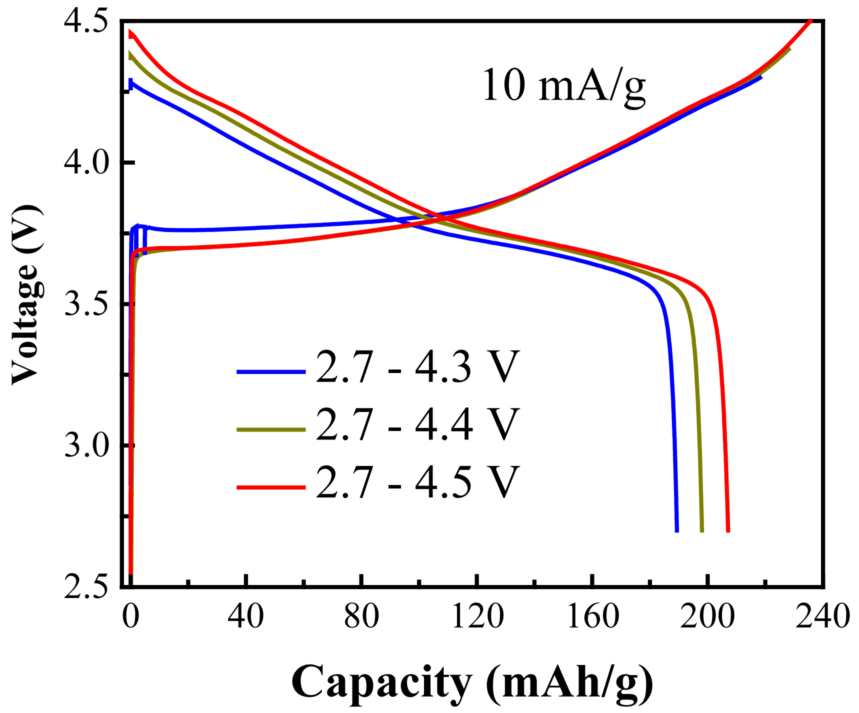
The average composition:
$\sim LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$
Outer: $\sim LiNi_{0.46}Co_{0.23}Mn_{0.41}O_2$
Inner: $\sim LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$

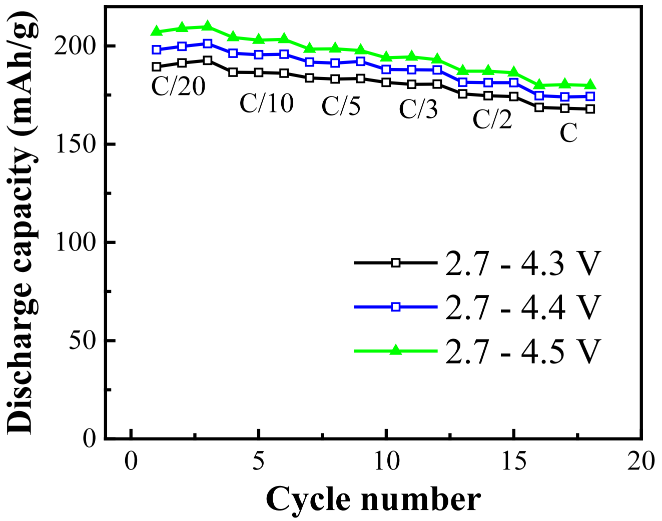
FCG (6:2:2) : $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$

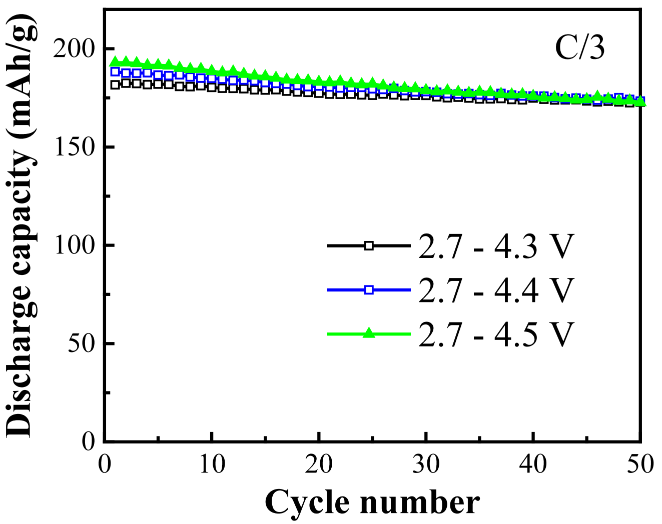
High tap density: 2.7 g/cc
particle distribution: D50=11.64 um

Electrochemical performance of FCG cathode at different cut-off voltages

- 2.7 – 4.3 V (192 mAh/g)
- 2.7 – 4.4 V (198 mAh/g)
- 2.7 – 4.5 V **(210 mAh/g)**

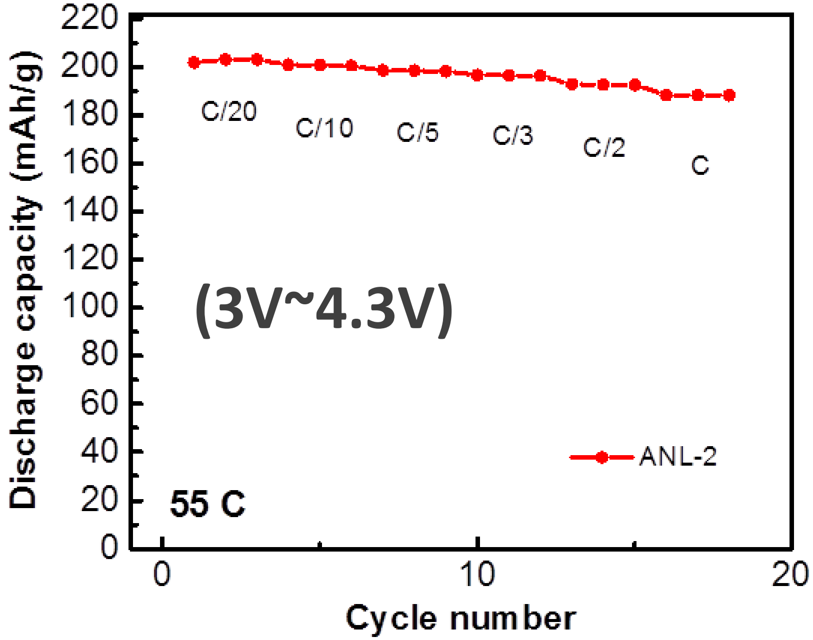


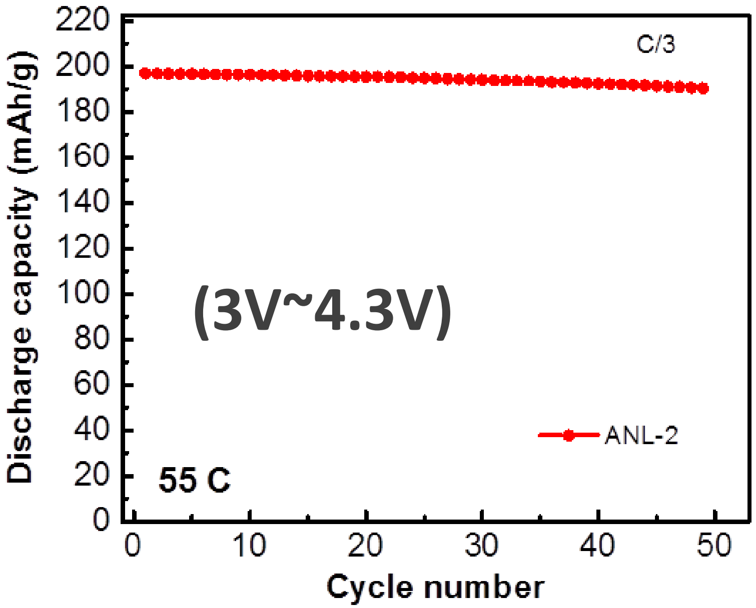




Electrochemical performance of FCG cathode at 55^oC

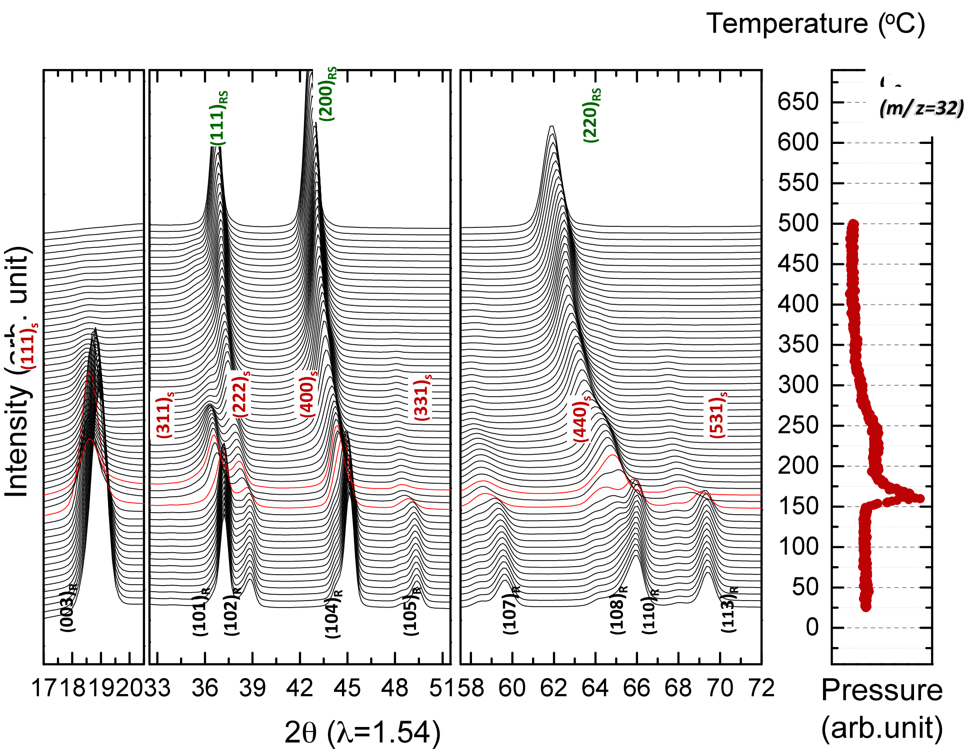
ANL-2 (FCG-6:2:2)



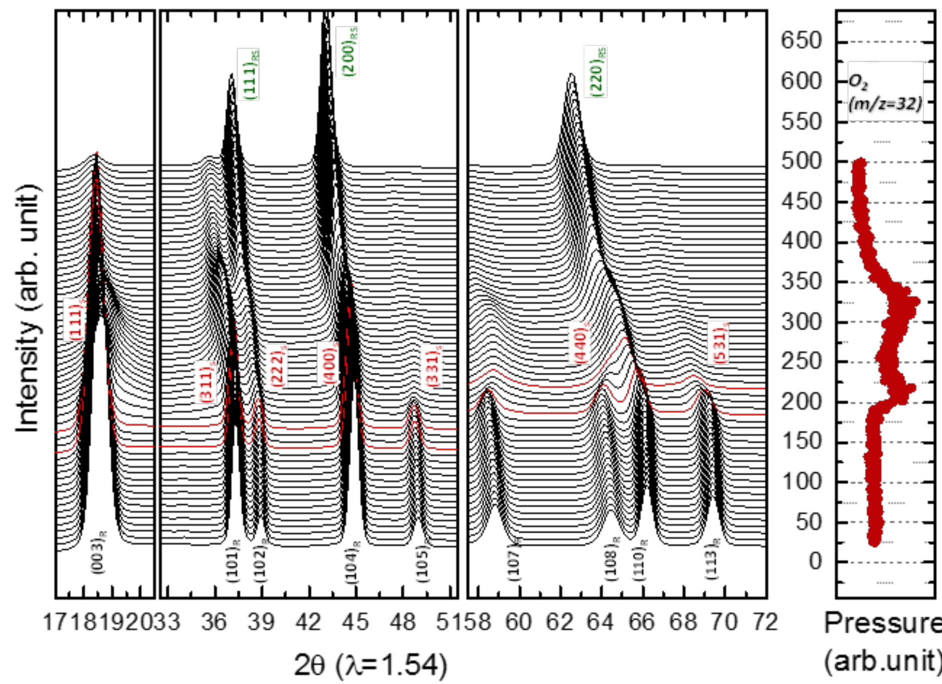


Excellent cycling stability at 55^oC

TR-XRD/MS of FCG (6:2:2) and NMC (6:2:2) baseline



$LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ (Baseline NMC 622)

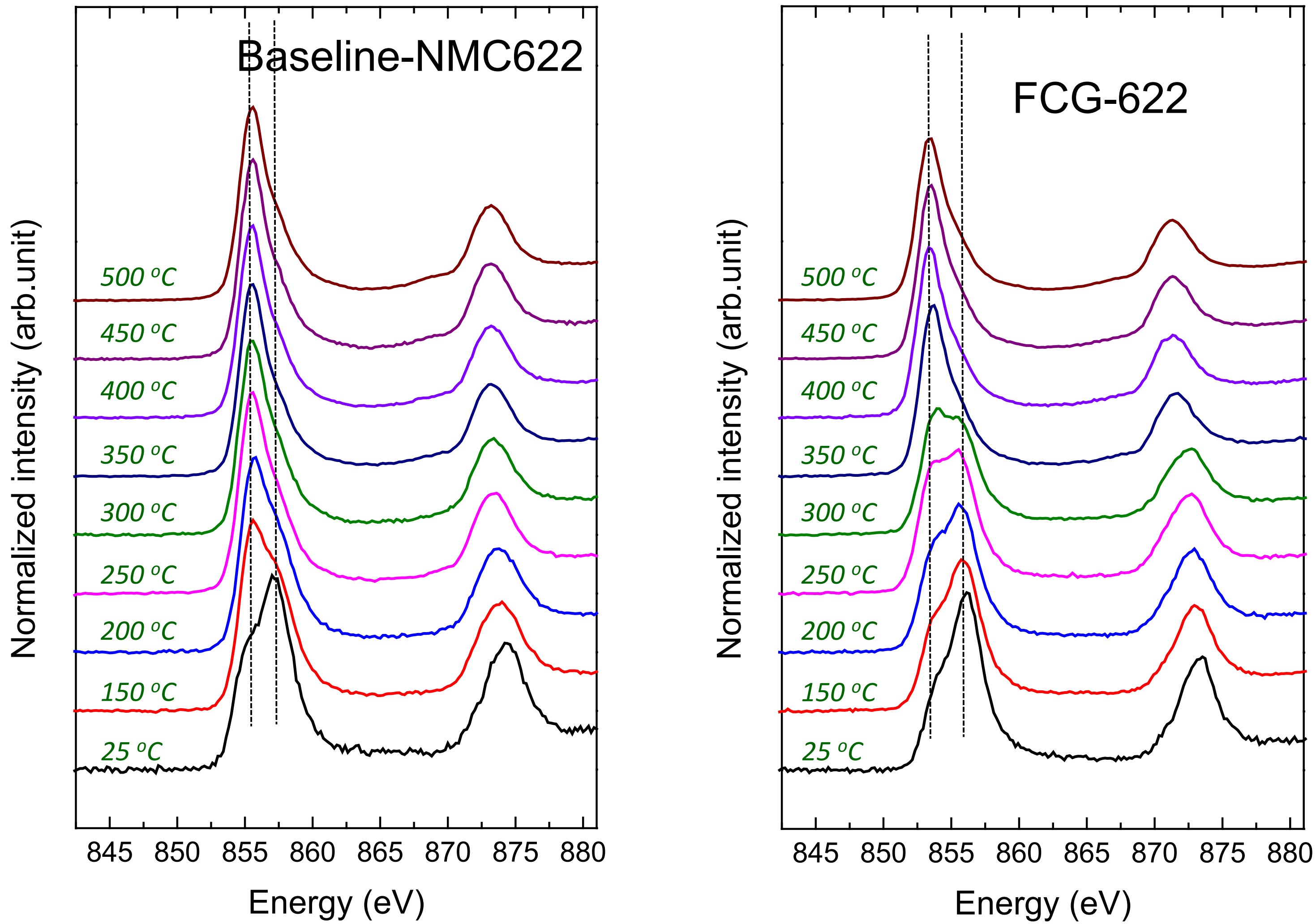


$LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$ (FCG-6:2:2))

- Sharp O_2 gas release (at *ca.* 150 °C) during phase transition from layered to disordered spinel phase

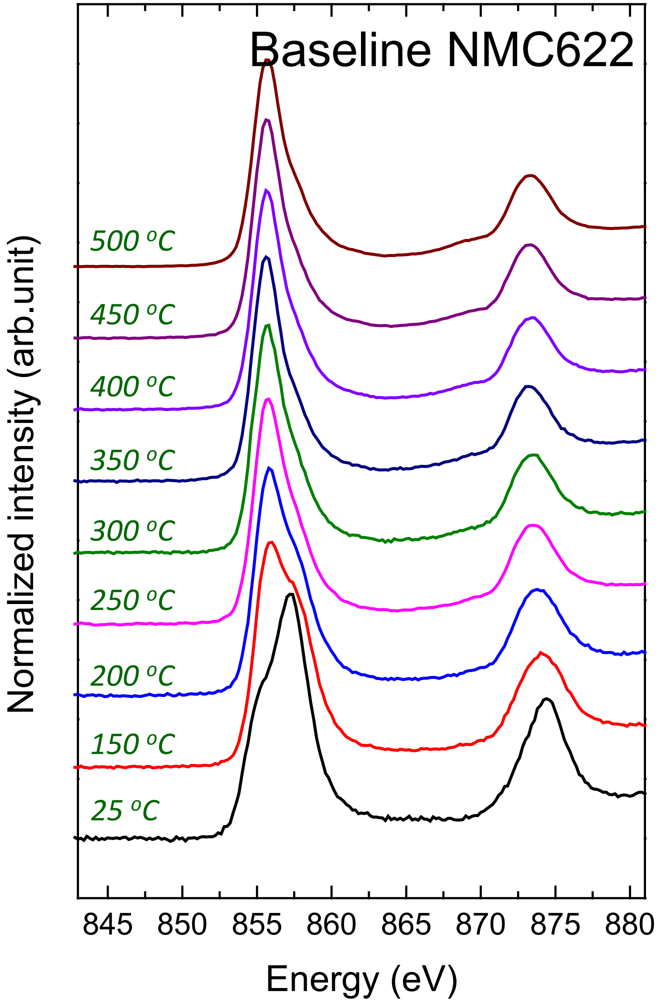
-Concentration gradient (FCG) sample shows much better thermal stability than baseline NMC 622
: 1st phase transition occurred at ca. 190 °C

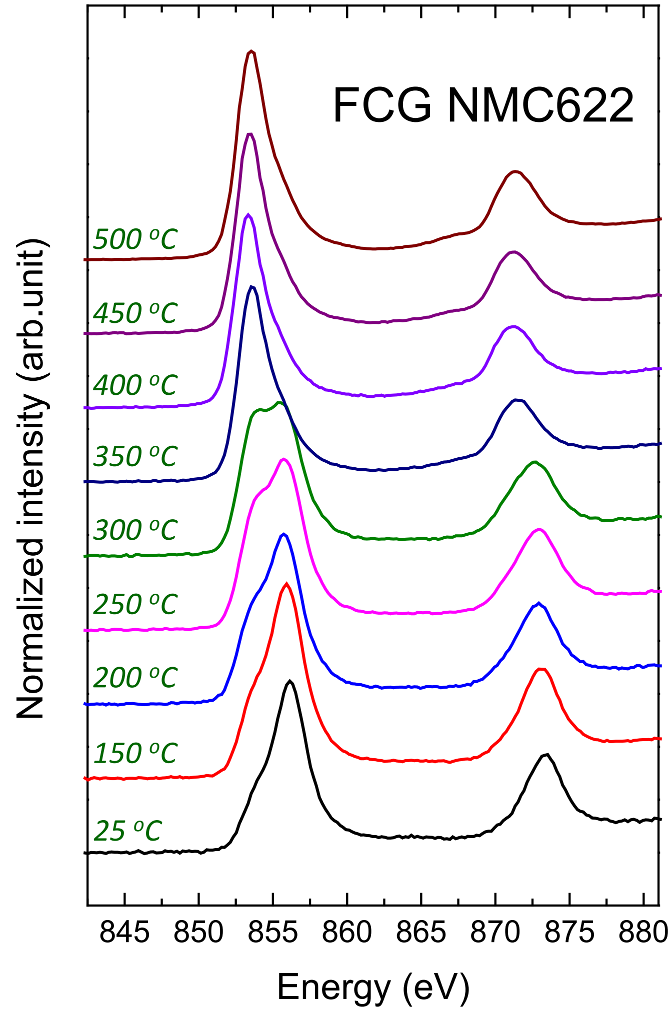
Ni L-edge soft XAS for baseline NMC622 (left) and FCG-622 (right) Using Fluorescence detection (FY, bulk probing)



Ni reduction reflected as the lower energy peak occurred quickly at low temperature (~150 °C) in baseline NMC622. In contrast, FCG-622 is more stable and Ni is stable up to 250 °C and gradually reduced, and completed at 350 °C

Ni L-edge soft XAS for Baseline NMC622 (left) and FCG (right) Using partial electron yield detection (PEY, Surface probing)



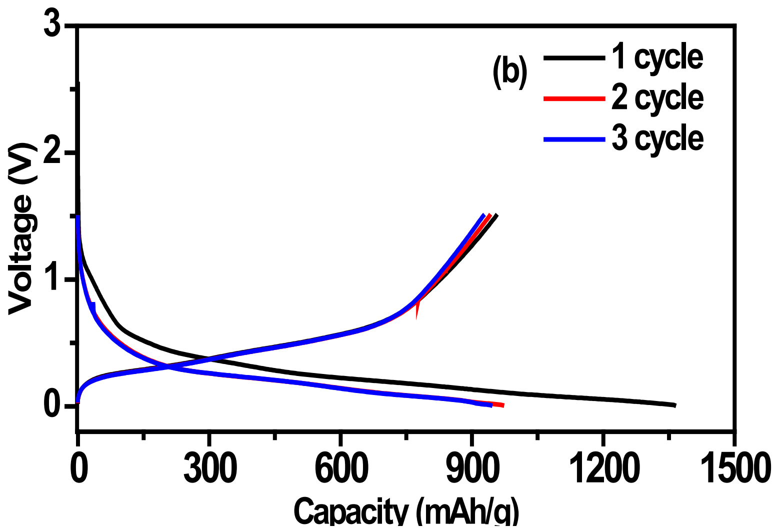


- The structural change at near surface also shows same trend with bulk structure.
- Ni reduction temperature is well coincident with the temperature of the phase transition and O2 release in TR-XRD/MS data

Optimization of SiO-SnCoC composite anode

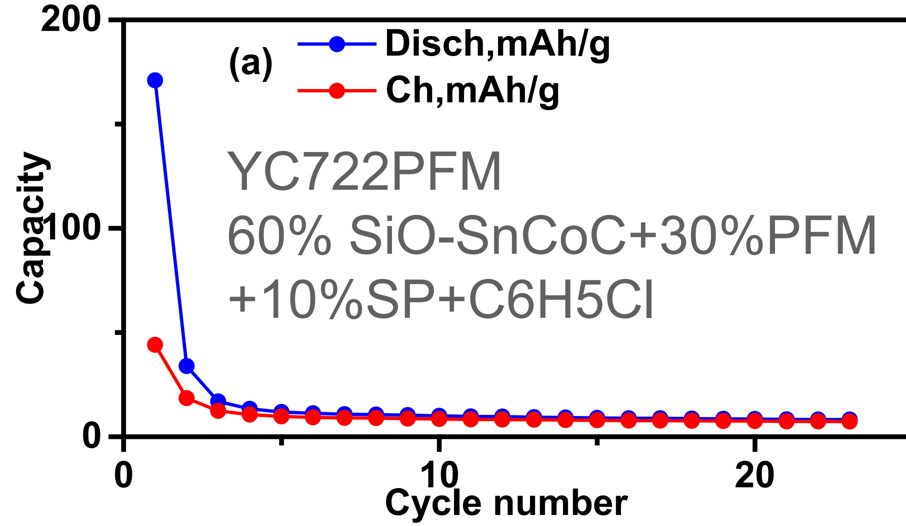
Main Issues:

Low efficiency:
65%~70%.



- Half cell SiO-SnCoC : 90/5%Timecal/5%PI
- Electrode loading: 2.5mg/cm^2
- 1st cycle reversibility between 70 to 72%.

Conductive binder (PFM) shows poor performance with Si-SnCoC composite



Approaches to resolving SiO-SnCoC composite anode issues

✓ Active material composition optimization:

- Mixing appropriate amount of graphite with SiO-SnCoC
- Best composition based on graphite mixing optimization is:

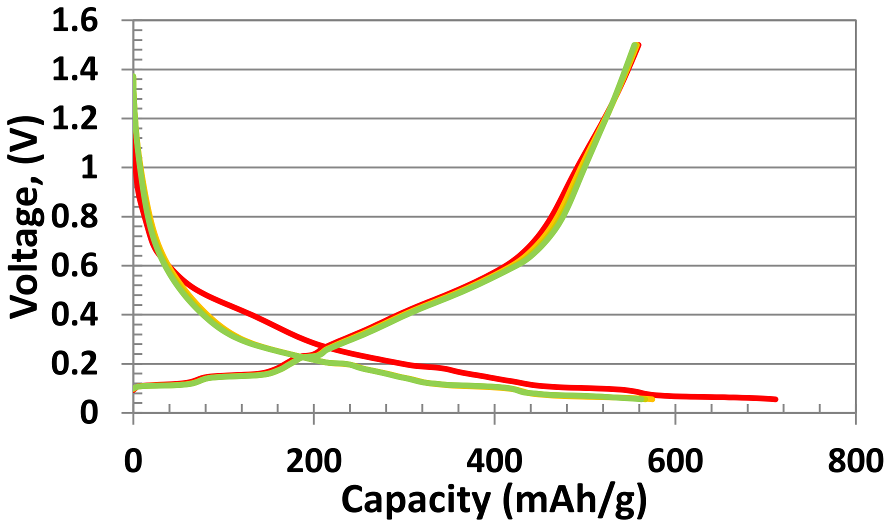
(33%SiO-SnCoC +57% MAG graphite)

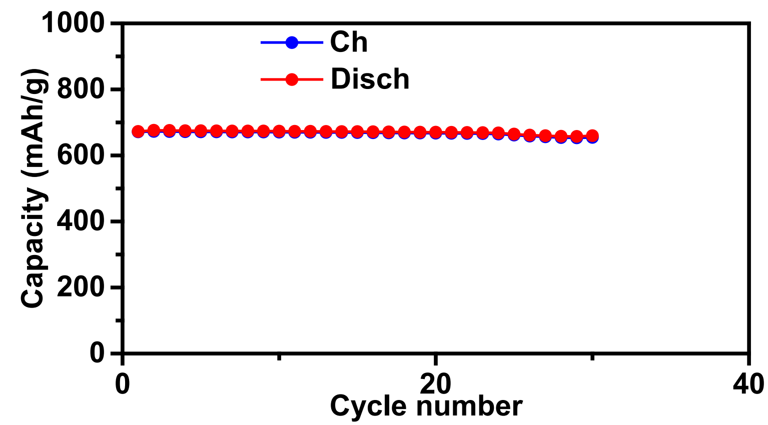
✓ Binder optimization:

- ✓ PFM conductive binder from LBNL
- ✓ PVDF
- ✓ Polyimide biner(PI)
- ✓ Polyacrylic acid binder (PAA)
- ✓ PVDF mix with PI
- ✓ PVDF mix with PAA
- ✓ LiPAA

33%SiO-$Sn_{30}Co_{30}C_{40}$/57%MAG graphite with 5%LiPAA shows the best performance with 81% 1st cycle efficiency

33% SiO-SnCoC+57%GC+5%LiPAA+5%C-45



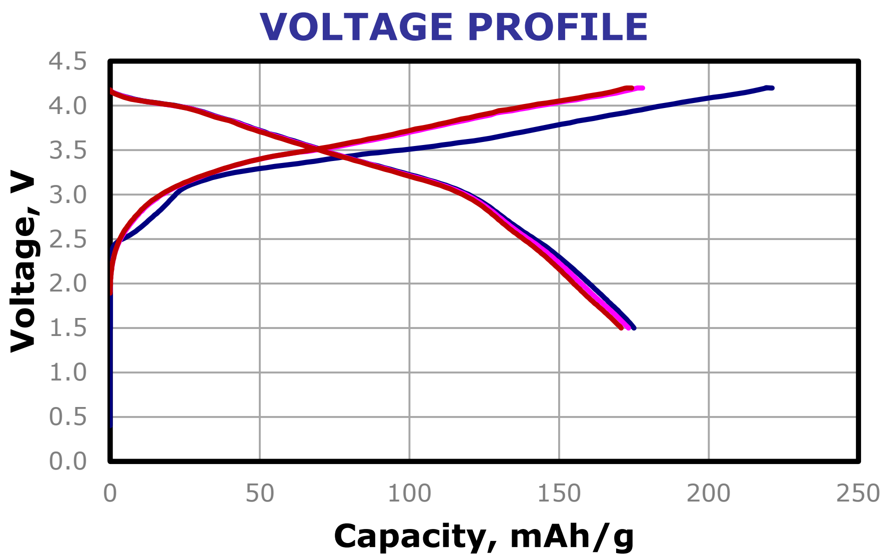


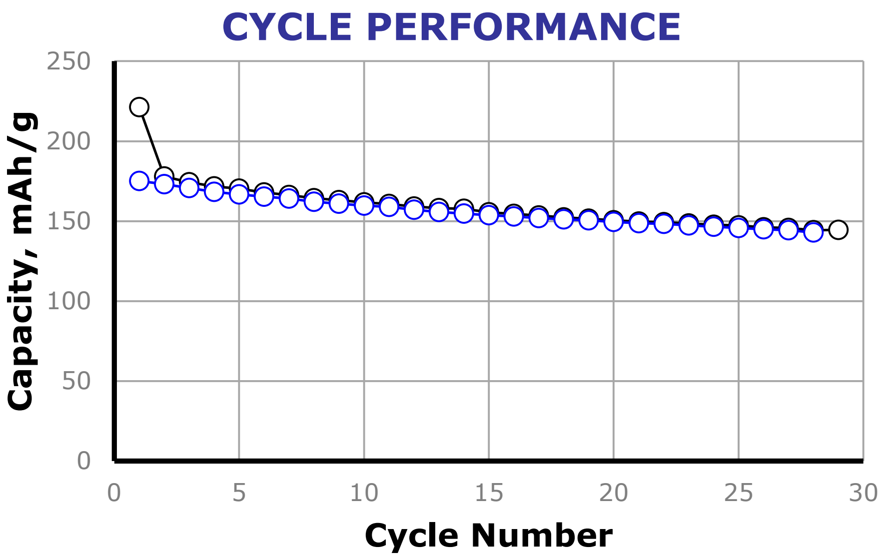
1st cycle C.E. 81 %.

1. The cell shows high 1st C.E. efficiency (81%).
2. The cell shows good rate performance.
3. The cell shows high capacity (670 mAh/g) and excellent cycle life so far.

33%SiO-$Sn_{30}Co_{30}C_{40}$/57%MAG graphite /5%LiPAA/ 5%C-45 formulation was used by CAMP facility to fabricate electrode for cell build

Initial performance of Full cell SiO-SnCoC-MAG/ FCG cathode

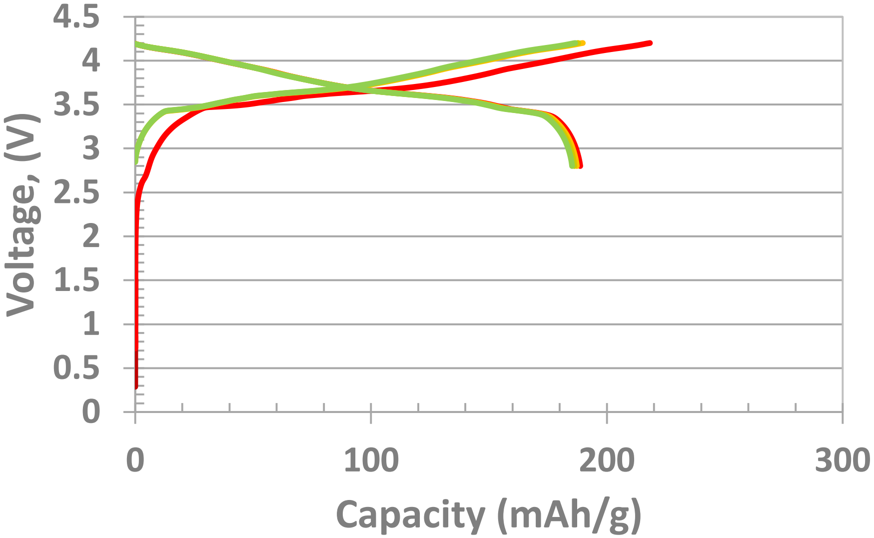


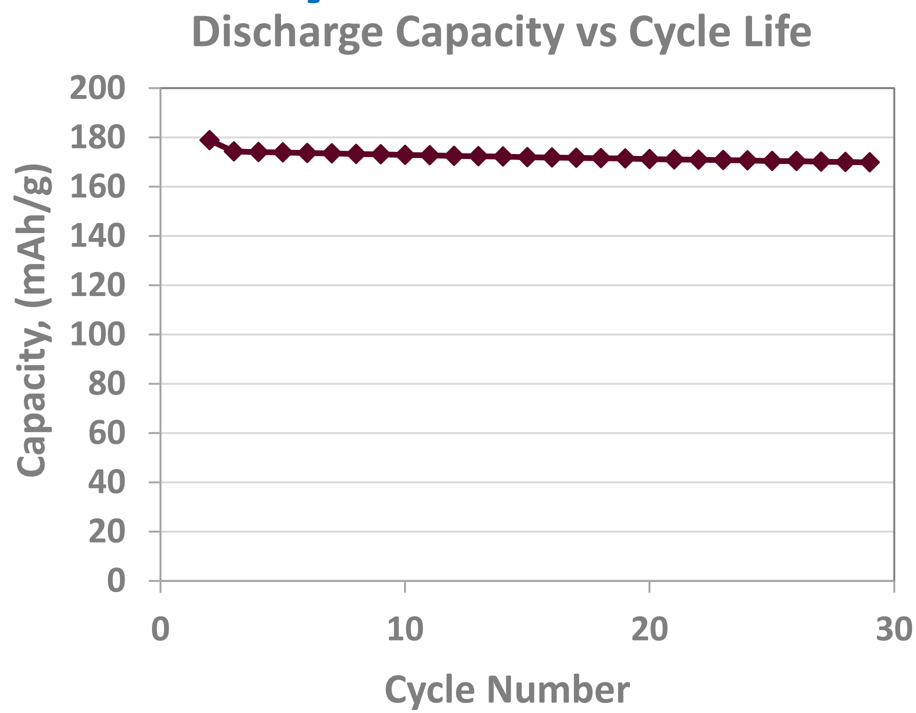


- The first discharge capacity is only 170mAh/g due to large initial irreversible loss of SiO-SnCoC-Mag anode

- Need to incorporate a pre-lithiation to maximize cathode capacity

Coupling FCG with Graphite instead of SiO-SnCoC-MAG shows excellent cycle life





1st C cap (mAh/g)	**218**
1st D Cap (mAh/g)	**189**
1st Cycle Eff (%)	**86.5**

By replacing SiO-SnCoC-MAG composite with graphite, the cycle life of the full cell with FCG cathode improved significantly,

Based on the result above, we decided to build FCG/MAG full cell while developing a pre-lithiation process to enable Si-SnCoC anode

Electrode Architecture and Cell Assembly based on FCG and MAG Graphite

- Pouch cell build is using
  - Anode (LN3012-178) -> MagE graphite
  - Cathode (LN3012-179) -> FCG
- Average Entire Cell Weight, as delivered: 11.0405 g

- Electrode Architecture
  - Cathode Electrode Dimensions : 31.3 mm W x 45.0 mm T
    - Cathode Electrode Area : 14.1 cm^2 per side
  - Anode Electrode Dimension : 32.4 mm W x 46.0 mm T
    - Anode Electrode Area : 14.9 cm^2 per side

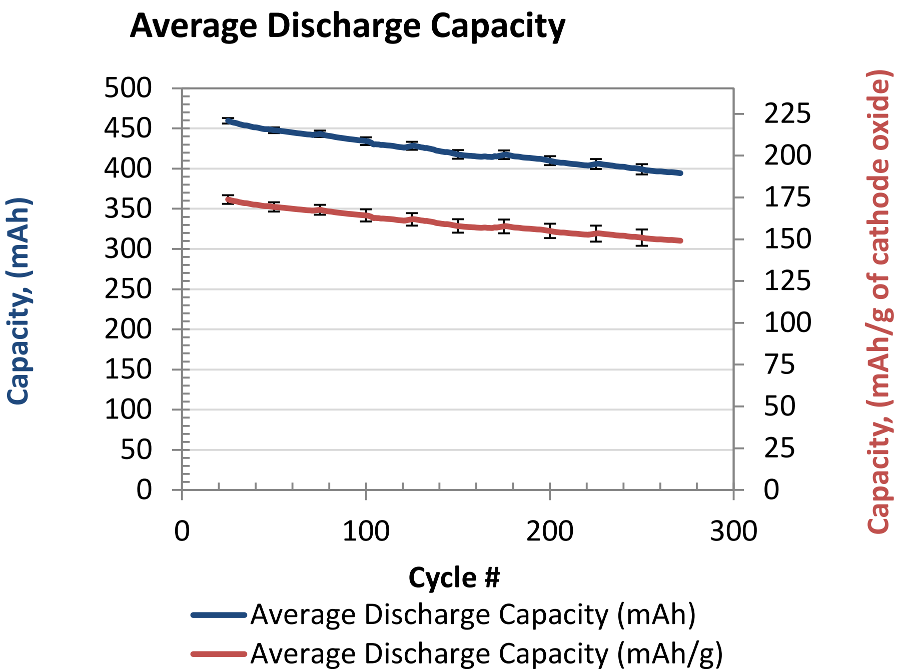
- Cell Assembly
  - Total Number of Layers : 13
    - Cathode Layers : 5 Double Side Layers + 2 Single Side Layers (outer 2 electrodes)
    - Anode Layers : 6 Double Side Layers
  - Separator Used : Celgard 2325 - Trilayer PP/PE/PP
  - Electrolyte Used : 1.2M $LiPF_6$ in EC:EMC (3:7 wt%)
  - Applied Cell Pressure during testing: ~15 kPa

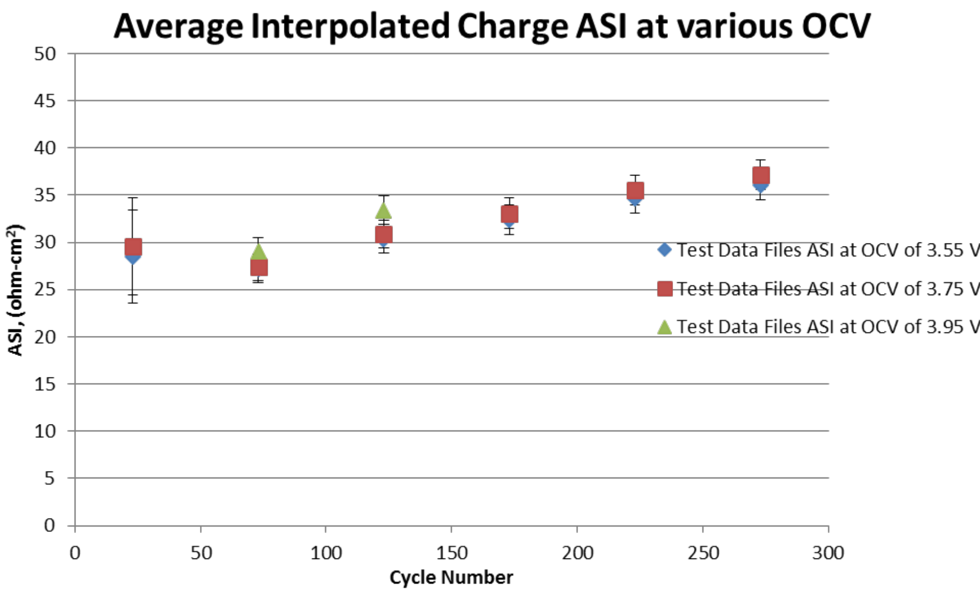
Cathode & Anode Formulation

- Cathode Formulation (Dry Composition)
  - 90 wt% FCG, Khal ABR 2014 (Lot 011915/012015)
  - 5 wt% Timcal C-45 Carbon Black
  - 5 wt% Solvay 5130 PVDF Binder
- Cathode Electrode Properties
  - Aluminum Foil Thickness: 20 microns
  - TTL DS Electrode Thickness: 159 microns
  - TTL SS Coating Thickness: 69 microns
  - Cathode Coating: 17.20 mg/cm² (SS)
    (Total Material wt; No Foil)
  - Capacity: 2.87 to 3.06 mAh/cm²
  - Target Porosity: 39.5 %
  - Coating Density: 2.47 g/cm³
- n:p Ratio: 1.10 to 1.16

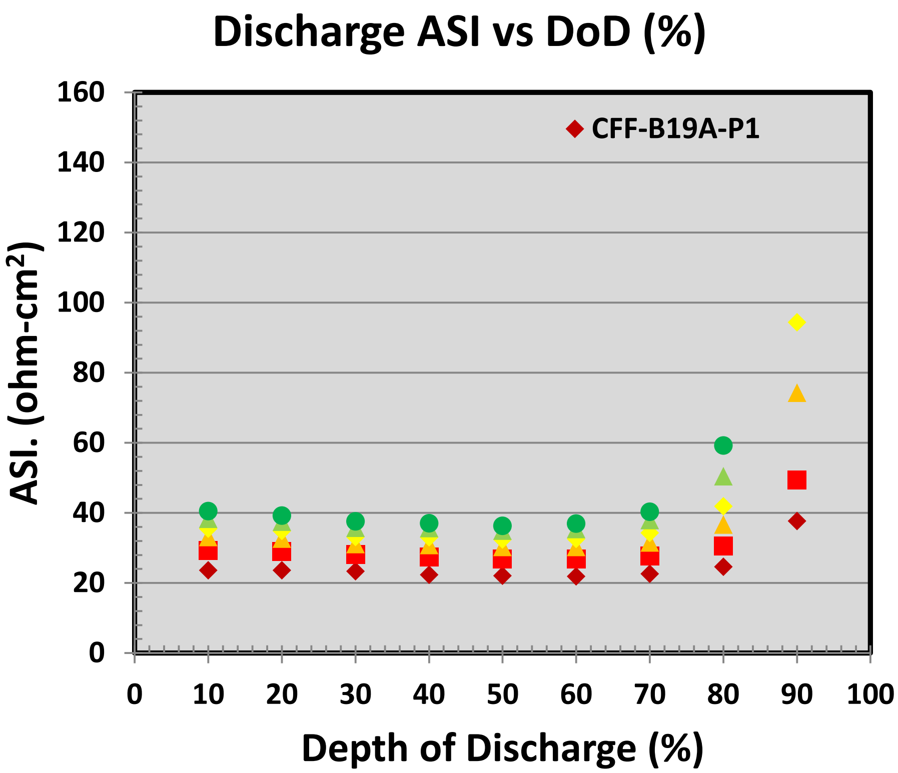
- Anode Formulation (Dry Composition)
  - 91.83 wt% Hitachi MagE
  - 2 wt% Timcal C-45 Carbon Black
  - 6 wt.% Kureha 9300 PVDF
  - 0.17wt.% Oxalic Acid
- Anode Electrode Properties
  - Copper Foil Thickness: 10 microns
  - TTL DS Electrode Thickness: 162 microns
  - TTL SS Coating Thickness: 76 microns
  - Anode Coating: 11.33 mg/cm² (SS)
    (Total Material wt; No Foil)
  - Capacity: 3.44 to 3.50 mAh/cm²
  - Target Porosity: 31.2 %
  - Coating Density: 1.49 g/cm³

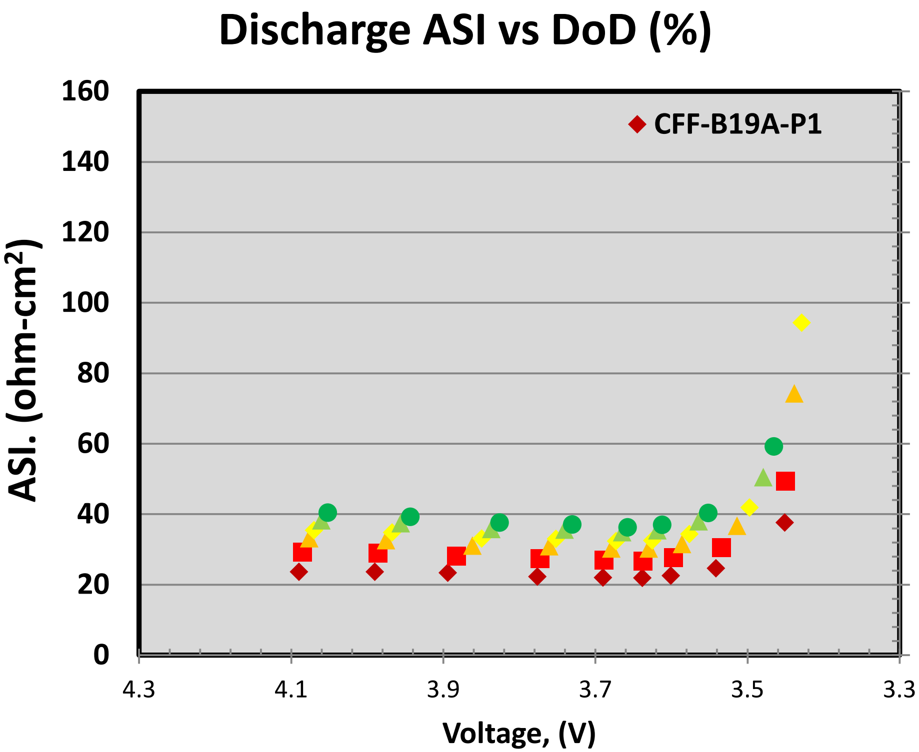
Initial performance of full cell based FCG (6:2:2) /MAG





Discharge ASI vs DOD of full cell based FCG (6:2:2) /MAG





Color	Cycle # Range
Red	20 to 70
Orange	120
Yellow	170
Green	220 to 270

Energy and power of baseline and FCG cells based on BatPac Design

Deliverable	Device	Battery Performance (Cell Level)			
		Usable Specific Energy (Wh/kg)	Energy Usable Density (Wh/l)	Power at SOCmin (W/kg,10sec)	Technology Info
*Baseline	20Ah Cell 40Ah Cell BatPac Design	(~199) (~237)	(~453) (~548)	(~1591) (~950)	SiO-SnCoC And NMC (6:2:2)
Gen1	20Ah Cell 40Ah Cell BatPac Design	(~229) (~280)	(~541) (~659)	(~1837) (~1120)	SiO-SnCoC-MAG And FCG (6:2:2)

* Data provided on baseline last year was higher than the one in the table above as we found a mistake in the Pat Pac model input.

Pre-lithiation of SiO-SnCoC to reduce the negative impact of large initial irreversible lose

ANL discover a new approach to pre-lithiation by activating Li_2O at the cathode side at high voltage

- Li_2O : Li sources to compensate for lithium consumption in lithium-ion batteries (improve fist cycle irreversibility of silicon and other anodes) (capacity of Li_2O ~ 1650 mAh/g)

- Li_2O could be combined with all cathodes non-containing Li such as: S; MnO2, V2O5, FeF3, SeSx……

LIB in the market is anode limited battery

- To balance battery with Graphite (CE:90%):

1 g of graphite delivers 3.2 mAh and needs 2 (+10%)= 2.2g of cathode material with (160 mAh/g) to have a cell with 3.2 mAh. (0.2 g of the cathode is a dead weight in the battery).

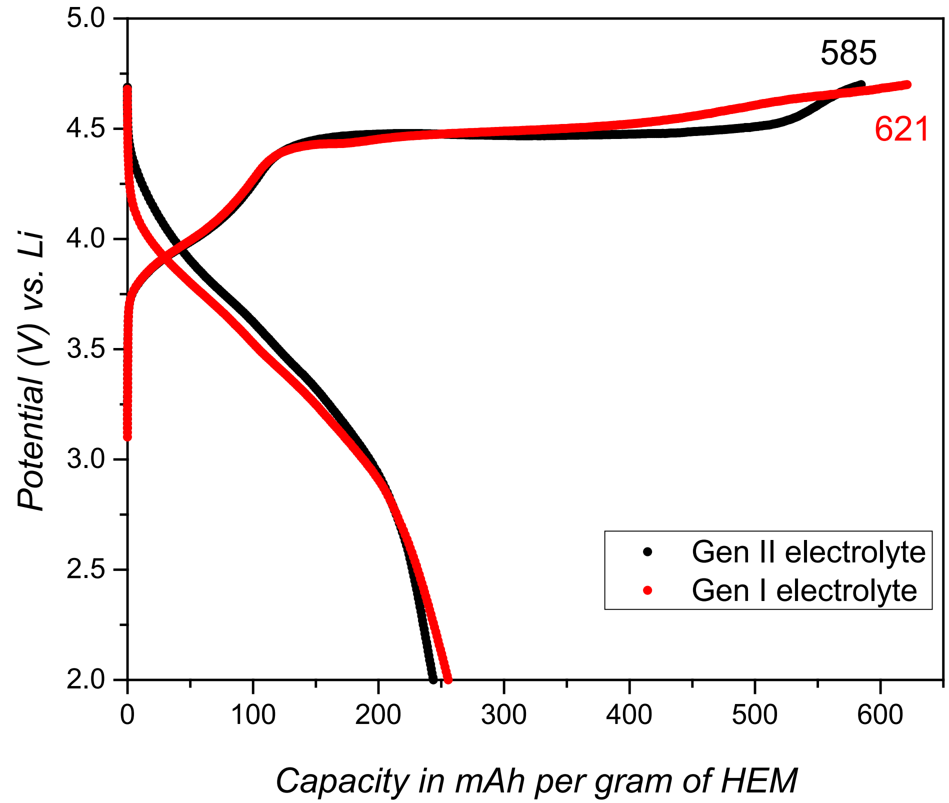
- To balance battery with Graphite/Silicon (CE:80%, capacity 728 mAh/g):

1 g of graphite/silicon delivers 6.4 mAh and needs 4 (+20%)= 4.8g of cathode material with (160 mAh/g) to have a cell with 6.4 mAh. (0.8 g of the cathode is a dead weight in the battery).

Li_2O with HEM electrode

HEM: $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$

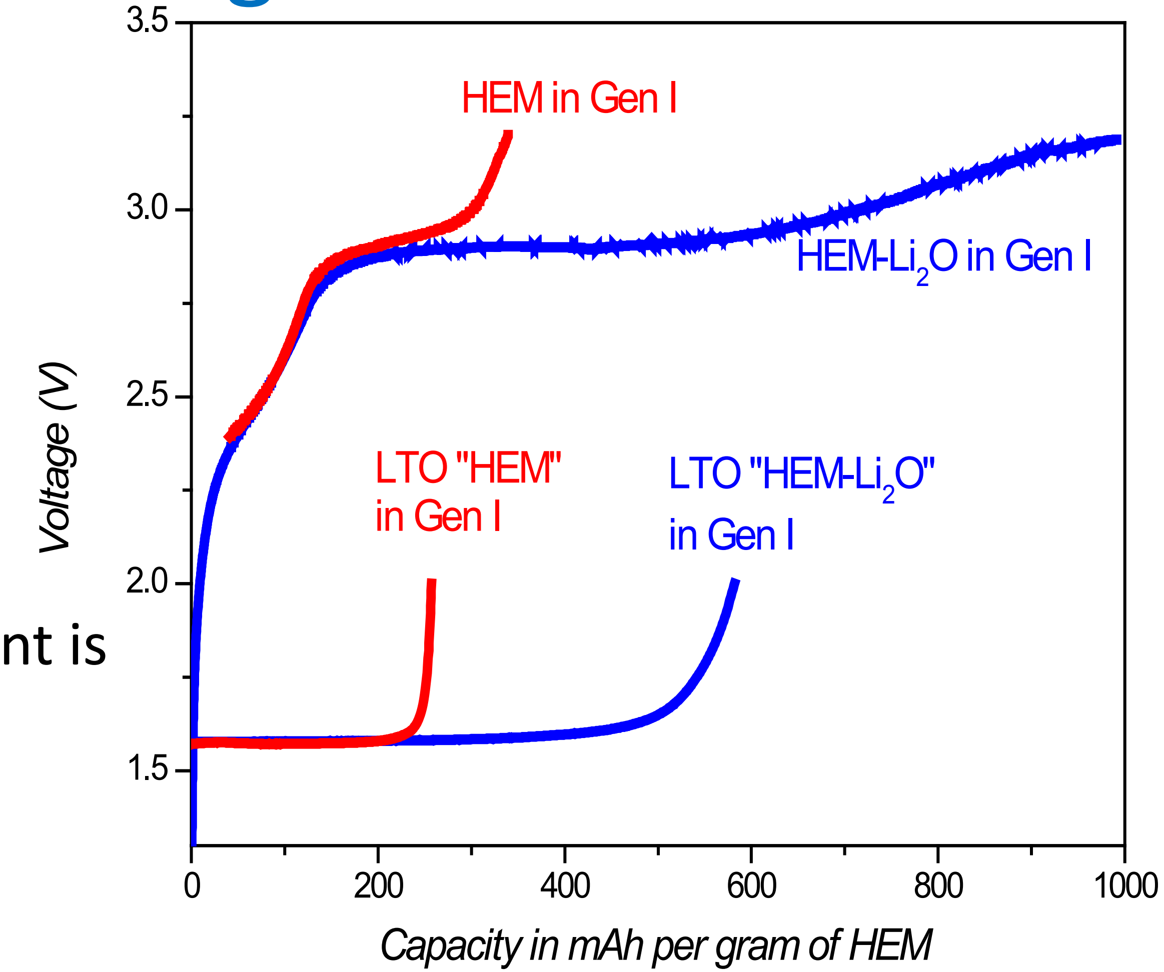
- High charge capacity is obtained when adding 15%Li_2O. Two times the charge capacity of the HEM material.
- Gen I: $LiPF_6$/EC:EMC (3:7)
- GenII: $LiClO_4$/EC:EMC (3:7)



Voltage profile versus capacity of HEM-Li_2O/Li half-cell with Gen I and Gen II electrolytes (I = 10 mA/g).

Proof of activation : amount of Li in the full cell using LTO anode

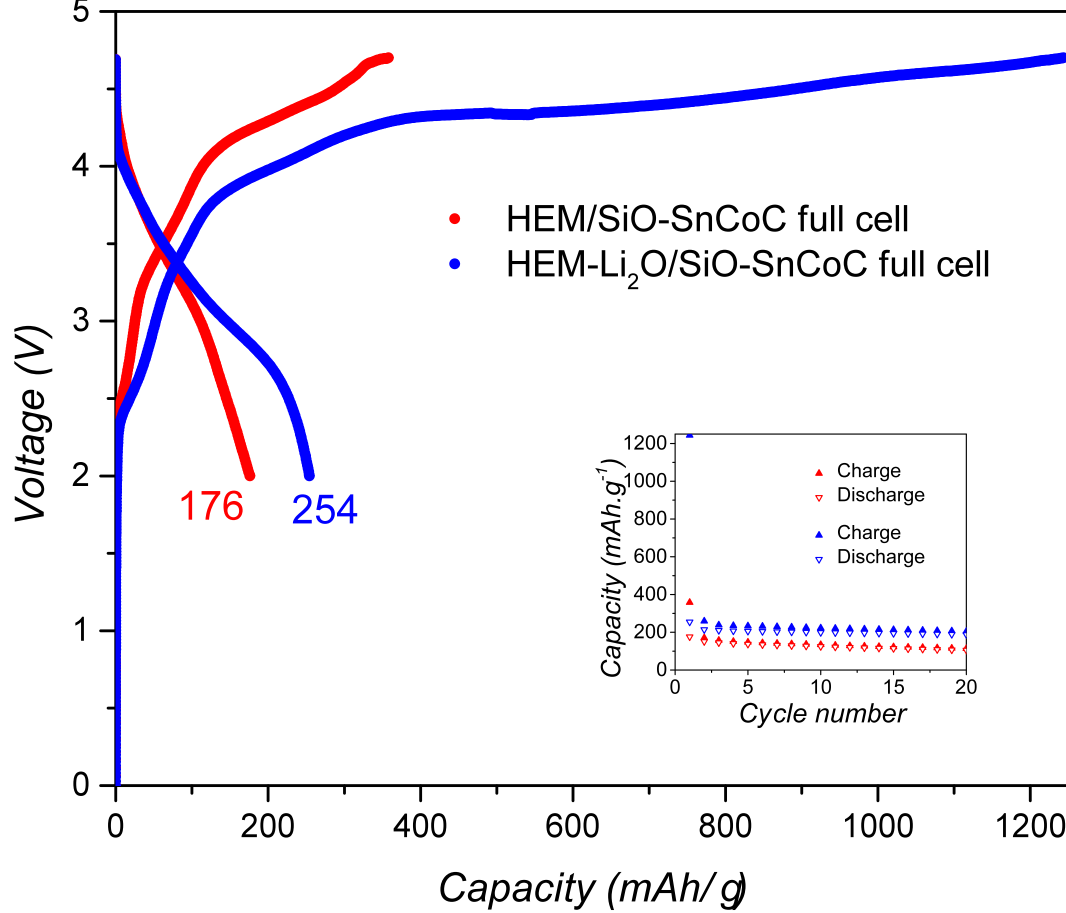
- The amount of lithium inserted in the LTO (from HEM-Li_2O) in mAh/g equivalent is 600 mAh/g.
- The amount of lithium inserted in the LTO (from HEM) in mAh/g equivalent is only 275 mAh/g.



Voltage profile versus charge capacities of HEM/ LTO and HEM-Li_2O/LTO full cells (I = 3 mA/g) and recovered LTO/Li half-cell in Gen I electrolyte (I = 8 mA/g).

2nd proof of concept with full cell SiO-SnCoO material with low CE ~66-70%

- The full cell capacity was improved from 176 mAh/g to 254 mAh/g.
- No effect on the cycling of full cells or half cells.
- The higher first charge shows no need of using a lot of Li_2O.



First-cycle voltage profile versus capacity and cycling performance (inset) of HEM–Li_2O/SiO-SnCoC and HEM/SiO-SnCoC full cells.

Responses to Previous Year Reviewers' Comments

- Question: reviewer 2 The anode material target of 900 mAh/g, the reviewer said, can be sufficient for the DOE PHEV-40 target. It would be of additional benefit, the reviewer concluded, to investigate the potential of the material to exceed 1,000 mAh/g and thus also to address EV application !
- Answer: the reviewer is absolutely righ. However, the targeted energy density in this project is 200wh/kg and we believe less than 900mAh/g anode capacity can easily meet this target

- Question : reviewer No:4 The key barriers that must be addressed, the reviewer stated, is long calendar and cycle life, but it is not clear how to address this challenge. In particular, the reviewer said, a solution for the instability of the SEI layer and attack by dissolved Mn from the surface of the FCG cathode to the anode side were not clearly discussed or planned. Also, the current anode system shows poor capacity and cycle life, problems the reviewer said could not be solved by addressing only the binder
- Answer: the issue of Mn dissolution and its imp[act on the SEI of the anode was resolved by adding LiBDOF electrolyte additive that resist any attack by Mn dissolution. In the past we have demonstrated 1000 cycle with 91% retention using FCG/MCMB.
- The Si anode we developed can provide very high capacity, however, we blend it with large amount of carbon to get 600mAh/g that we believe can meet the 200wh/kg energy requirement. The cycle life vs lithium is excellent , however, the cycle life in full cell was not satisfactory because of the difficulty of CAM lab to make good electrodes during scale up!

Responses to previous year reviewers' comments

- Question: reviewer 1: the Nickel contact on FCG should increase to get high capacity.
- Answer: we totally agree with the reviewer. The development of Ni rich gradient will require more time to optimize the gradient slop. This will be the subject of a different project that we hope will be supported by DOE.

Collaborations

- X.Q. Yang of BNL
  - Diagnostic of FCG and SEI of Si-Sn composite electrodes using soft & hard X-ray.

- G. Liu (LBNL)
  - Development and optimization of conductive binder for Si-Sn composite anode

- H. Wu (ANL)
  - Optimize the synthesis of FCG cathode

- A. Abouimrane (ANL)
  - Development of $SiO\text{-}Sn_yCo_{1-x}Fe_xC_z$ anode

- J.Lu & Z. Chen (ANL)
  - Characterization of cathode, anode and cell during cycling using In-situ techniques

- ECPRO : Baseline cathode material

- University of Utah : Facility to scale up the baseline Si-Sn composite anode for baseline cell

- A. Jansen & B. Polzin (ANL)
  - Design & fabrication of baseline cell

Summary

- ## Relevance
  - enable low battery cost by increasing energy density
  - Low battery cost will lead to mass electrification of vehicle and reduction of both greenhouse gases and our reliance on foreign oil
- ## Approaches
  - develop very high energy redox couple (250wh/kg) based on high capacity full gradient concentration cathode (FCG) (210mAh/g) and Si-Sn composite anode (670mAh/g) with long cycle life and excellent abuse tolerance to enable 40 miles PHEV and EVs
- ## Technical Accomplishments
  - Optimize the process of making FCG cathode and demonstrate capacity as high as 210mAh/g with 2.7 tap density
  - Scale up FCG cathode to 1Kg level for electrode making using CAMP facility at Argonne
  - Improve the efficiency of SiO-Sn_{30} $Co_{30}C_{40}$ anode to 81% by Developing SiO-Sn_{30} $Co_{30}C_{40}$ –MAG graphite composite formulation and scale up the new composite to 1Kg level.
  - Develop a novel pre-lithiation process to overcome the first irreversible loss at the Si0SnCoC anode
- ## Proposed Future work
  - The project ended at the end of September 2015